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Hydrochemistry, mineralogy and chemical fractionation of mine and processing wastes associated with porphyry copper mines: A case study from the Sarcheshmeh mine, SE Iran

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ABSTRACT

The Sarcheshmeh is one of the largest Oligo-Miocene porphyry Cu deposits in the world. Comparative hydrochemical, mineralogical and chemical fractionation associated with mining efflorescence salts and processing wastes of this mine are discussed. Hydrochemical results showed that rock waste dumps, reject wastes and old impoundments of tailings are the main sources of acid mine drainage waters (AMD) that contain potentially toxic metals such as Cd, Co, Cu, Mn, Ni and Zn as well as Al. Episodic fluxes of highly contaminated acidic waters were produced in a tailings dam over a short period of time. Secondary soluble minerals provide important controls on the quality of AMD produced, especially in old, dry tailings impoundments. Secondary sulfate minerals such as gypsum, magnesiocopiapite, hydronium jarosite, kornelite and coguimbite were found in rock waste drainages and in old weathered reject wastes. Highly soluble secondary minerals such as gypsum, eriochalcite, and bonattite are also observed in an evaporative layer on old tailings impoundments. Chemical fractionation patterns of potentially toxic elements showed that the geochemical behavior of metals is primarily controlled by the mineralogical composition of waste samples. Elements such as Co, Cr, Cu, Mn, Ni and Zn are readily released into the water soluble fraction from efflorescence salts associated with rock waste drainages, as well as from the evaporative layer of old tailings. Potentially toxic elements, such as As, Mo and Pb, are principally adsorbed or co-precipitated with amorphous and crystalline Fe oxides, but they may also be associated with oxidizing, primary sulfides and residual fractions. Following the development of the dammed tailings pond, the secondary minerals were dissolved, producing acidic waters contaminated by Al (154 mg L⁻¹), Cu $(150 \text{ mg L}^{-1}), \text{ Cd } (0.31 \text{ m gL}^{-1}), \text{ Co } (2.13 \text{ mg L}^{-1}), \text{ Mn } (73.7 \text{ mg L}^{-1}), \text{ Ni } (1.74 \text{ mg L}^{-1}), \text{ Zn } (20.3 \text{ mg L}^{-1}), \text{ Mn } (20.3 \text{ mg L}^{-1}), \text{ Ni } (20.3$ and Cl (1690 mg L⁻¹). Therefore, the potential use of recycled water from the Sarcheshmenh dammed tailings pond is diminished by the presence of corrosive ions like Cl- in highly acidic fluids that promote corrosion of pipes and pumps in the water recycling system.

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1. Introduction

Porphyry deposits are the principal sources of Cu and Mo in the world. They are relatively low grade, epigenetic, intrusion-related deposits that can be mined using mass mining techniques (Lowell and Guilbert, 1970; Gustafson and Hunt, 1975; Cox et al., 1995; Berger et al., 2008; Singer et al., 2008). Studies have shown that trace metals and metalloids such as Cu, Mo, Au, Ag, Ba, Pb, Zn, As, Sb and Te make up geochemical suites related to alteration zoning within porphyry Cu deposits (e.g. Beus and Grigorian,

1977; Chaffee, 1982, 1992, 1994). The principal associations are Cu–Mo–Au ± Ag–As and Ba–Zn–Pb–Sb–Ag–As–Tl ± Bi (Berger et al., 2008).

Most porphyry Cu deposits are mined by open-pit methods and, less commonly, by underground methods (Berger et al., 2008). Beneficiation of the ore deposits is accompanied by high volumes of various metal rich wastes that are the most important potential hazard to the environment (Dudka and Adriano, 1997; Herr and Gray, 1997; Gray, 1997; Lottermoser, 2003). Mining and mineral processing are the two principal sources of the solid wastes in the mining industry (Lottermoser, 2003). Volumes of waste rock will depend upon the depth and geometry of the deposit as well as the competency of the country rock as it relates to stripping ratios. On average, about 1.5 tons of waste rocks and overburden

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must be removed for every ton of ore grade mined in porphyry Cu deposits (Phillips and Niemuth, 1993). Grades and tonnages for these deposits are detailed by Singer et al. (2008).

Several authors have discussed the geo-environmental features of porphyry Cu deposits (Learned, 1972; Chaffee et al., 1981; Eychaner, 1991; Stollenwerk, 1994; Cox et al., 1995; Brown et al., 1998; Lind et al., 1998; Conklin et al., 2001; Gammons and Duaime, 2005; Gammons et al., 2005; Plaza-Toledo, 2005; Leybourne and Cameron, 2006; Enders et al., 2006). Several reports have also compiled environmental and geological data to provide an initial prediction of potential impacts from sulfide-bearing mine wastes (Ficklin et al., 1992; Plumlee, 1994; Bowell et al., 2000; Hansen et al., 2005).

While the sulfide-bearing rocks are exposed to O2 and water they produce acid mine drainage, liberate the sulfide mineral constituents, and form secondary minerals (Luther, 1987; Alpers et al., 1994: Evangelou, 1995: Nordstrom and Alpers, 1999a: Plumlee, 1999; Jambor et al., 2000; Verplanck et al., 2009). The role of secondary minerals in the release of metals and acidity and for assessing the environmental risk of toxic metals has already been investigated (e.g. Cravotta, 1994; Jambor et al., 2000; Gieré et al., 2003; Bowell and Parshley, 2005; Elisa et al., 2006). A decrease in pH is principally caused by the dissolution of Fe²⁺ sulfate salts, which are capable of producing acidity due to hydrolysis of Fe. Secondary minerals can be classified as readily soluble, less soluble, and insoluble (Lottermoser, 2003). Therefore, the type of secondary minerals formed can profoundly affect the release and transport of toxic metals during the sulfide mineral oxidation processes. For example, dissolution of some secondary soluble mineral phases such as Fe²⁺, Mn²⁺, Fe³⁺ and Al³⁺ sulfate salts (e.g., jarosite or halotrichite) can release H⁺ and metals into the water (Plumlee, 1999; Nordstrom and Alpers, 1999b; Cravotta, 1994).

Beside the primary mineralogy of the wastes, climate is another factor that controls the secondary mineral formation. Understanding of the effects of various climate regimes on the geo-environmental signatures specific to porphyry Cu deposits is limited (Dold and Fontboté, 2001; Berger et al., 2008). Dold and Fontboté (2001) concluded that climatic variations especially the evaporation and precipitation cycle of water provide fundamental controls on the mobility of metals.

Mobility of toxic metals is a crucial factor for evaluating the short and long-term environmental impacts associated with mine wastes, because it has been demonstrated that high trace metal concentrations may not readily be mobile or bioavailable (Williams et al., 1999). Chemical fractionation analyses, combined with mineralogical studies, have been increasingly applied to mine waste samples (Ribet et al., 1995; Fanfani et al., 1997; McCarty et al., 1998; Dold and Fontboté, 2002; Lacal et al., 2003; Dold, 2003) for determining the mobility and complex processes present in mine waste, such as sulfide oxidation and subsequent retention of mobilized elements. Comprehensive, fundamental reviews have been published that summarize the mechanisms of chemical fractionation of metals in secondary solids (Filgueiras et al., 2002; Gleyzes et al., 2002; Hlavay et al., 2004).

To date, no study has been implemented on the type of secondary mineral phases and their roles in metal retention, release and transport in the wastes related to the Sarcheshmeh porphyry Cu deposit. This subject is important for environmental risk assessment of mining activities in this area. The aim of this study was to investigate the hydrochemistry, mineralogy and chemical fractionation of mine and processing wastes in the water–sediment systems related to rock waste drainage and concentration plant wastes at the Sarcheshmeh porphyry Cu mine. In this paper "potentially toxic elements" refers to the metals and metalloids that have been characterized as potentially toxic to life forms (Siegel, 2004).

2. Geology, mineralization and site characteristics

The Sarcheshmeh Cu mine is based on one of the largest porphyry Cu deposits in the world. The mine is located in the central Iranian volcanic–plutonic Cu belt, 160 km SW of Kerman (Fig. 1). The Sarcheshmeh area is located in an arid to semi-arid region with mean annual temperatures between -20 and 32 °C. The ore body, with dimensions of 2000 m by 900 m, contains 450 M tones of ore with average grades of 1.13% Cu and 0.03% Mo and a cutoff grade of 0.4% Cu (Waterman and Hamilton, 1975). The area is composed predominantly of Eocene-aged basic-to-intermediate volcanic host rocks that include trachybasalt, trachyandesite and/or andesite (Dimitrijevic, 1973) (Fig. 1).

The Sarcheshmeh Stock is a complex intrusive body, which is exposed over an area of about 1.2 km by 2.2 km. The diorite-to-granodiorite groundmass is fine-grained, and consists mainly of quartz, plagioclase and K-feldspar, with lesser biotite and amphibole. Dacitic and related pyroclastic dykes are pervasively altered, and contain abundant feldspar and amphibole phenocrysts in an aphanitic groundmass. Andesitic and related dykes consist mainly of plagioclase, K-feldspar, quartz and highly altered amphibole (Hezarkhani, 2006).

Mineralization is typically in stockworks and veins that are equally distributed between Eocene volcanics and Oligo-Miocene units of quartz diorite, quartz monzonite and granodiorite (Bazin and Hubner, 1969; Anon., 1973; Dimitrijevic, 1973; Etminan, 1977; Shahabpour, 1982; Atapour and Aftabi, 2007; Hezarkhani, 2006). Hydrothermal solutions released by sub-volcanic granodiorites have caused a lesser degree of mineralization in trachybasalt ± trachyandesite host rocks.

In the trachyandesite volcanic wall rocks, three different zones are observed that are concentric to the potassic and phyllic alterations of the Sarcheshmeh porphyry Stock (Shahabpour and Doorandish, 2007). The internal zone closest to the stock is characterized by strong biotitic and weak phyllic alteration. The intermediate zone is characterized by weak biotitic and strong phyllic alteration, and the external zone is very thick, grading at the periphery into unaltered country rocks (Shahabpour and Doorandish, 2007).

The volcanic–plutonic complex, also known as the Sarcheshmeh complex has less abundant andesite and rare occurrences of agglomerate, tuff, tuffaceous sandstone and less frequently, limestone (Atapour and Aftabi, 2007). Calcareous terraces and recent alluvium are the main sedimentary units formed in Quaternary times (Dimitrijevic, 1973).

Rock wastes and low grade oxide ores of the Sarcheshmeh deposit are usually dumped in the natural valleys around the mine. Some of these rock waste dumps generate acid mine drainage, especially in the wet seasons. The colorful yellow-red-brown precipitates (commonly referred to as "efflorescence") and filamentous algae that are typical for acid mine drainage are well observed in rock waste drainages (Fig. 2A and B). Secondary mineral phases are typically formed in dry months at the edge of acid mine drainage (AMD) affected drainages.

Nearly 0.97–1.79% of the primary feed of the beneficiation processes in the Sarcheshmeh Cu complex is removed as waste from a semi-autogenus mill. These materials are known as reject wastes. Approximately 10,000 tons of reject waste with an average grade of 0.6% Cu is produced annually. Sulfide minerals are observable in fresh gravel-size reject wastes, even with the naked eye. The reject wastes are typically highly porous and favorable for $\rm O_2$ and water infiltration. Intense oxidation of sulfide minerals results in release of large quantities of acid drainage from reject wastes into the environment (Fig. 2C and D).

Tailings constitute another type of processing waste that is produced in large volumes and accumulated in the Sarcheshmeh tailings dam, 18 km north of the mine (Fig. 1). Nearly

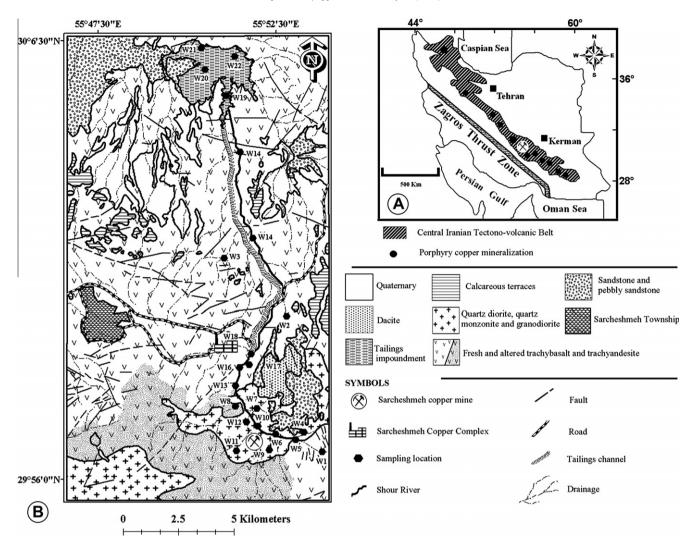


Fig. 1. (A) Central Iranian tectono-volcanic belt and location of the Sarcheshmeh porphyry Cu deposit (modified after Shahabpour and Kramers (1987)). (B) The Geological map of the mine district (modified after Dimitrijevic (1973)). The water sampling locations are also shown.

1,215,000 tons of tailings with an average Cu grade of 0.1% and Mo grade of 0.009% are produced annually in the Sarcheshmeh concentration plants. The tailings dam contains several impoundments, with a crustal layer of well developed secondary evaporative minerals at the top of dry impoundments (Fig. 2E). Tailings are suspended in a fine-grained sediment-water slurry. These wastes dominantly consist of the ground-up gangue, from which most of the valuable minerals have been removed by processing methods.

Waste water effluents and atmospheric emissions are the other contaminant sources associated with mineral processing in the Sarcheshmeh Cu mine.

3. Materials and methods

Field work included the identification and sampling of various surface water effluents, sediments and efflorescence salts associated with rock waste drainage, reject wastes, tailings and sediments related to waste water effluents from the concentration plants.

3.1. Water

Surface water effluents were characterized through analysis of samples collected at the 22 stations indicated in Fig. 2B. Parameters

such as pH and electrical conductivity (EC) of water were measured in the field by the use of a multiparameter device (Toledo MP-120 model) that was calibrated by standard solutions at pH = 4 and 7. Collected samples were immediately filtered through 0.45 μm filters (ALBET, Nitrato Celulosa, model), acidified with concentrated HNO3 (at pH < 2), and were stored at 4 °C until elemental analysis was performed. Filtered (0.45 μm filters) unacidified samples were also collected for anion analysis.

Major and trace element concentrations in water samples were determined using ICP-MS for As, Cd, Co, Cr, Cu, Mo, Ni, Pb, Zn and ICP-OES for Al, Fe, Mn, and S at Amdel Laboratory, Perth, Australia. Sulfate, HCO_3^- and Cl^- were determined by spectrophotometry, titration and Mohr's method, respectively.

3.2. Waste

Waste samples, including secondary mineral and efflorescence salts associated with rock waste drainage, old weathered rejects, surface and sub-surface tailings, and sediments related to the concentration plant effluents, were collected for mineralogical and chemical fractionation analyses. Samples were collected with a stainless steel device and were stored in air-tight plastic bags. For homogeneity control, nearly 5 kg of each sample were collected at each station. Samples were air dried and sieved; the <80 μm fraction was selected for analyses.

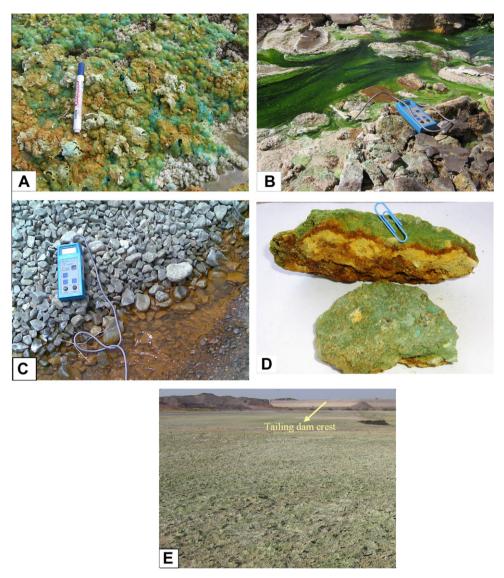


Fig. 2. (A and B) Field indicators of AMD processes in rock waste drainages; (C) AMD discharges from reject wastes after rainfall; (D) highly weathered old reject wastes; (E) a crust layer of secondary minerals on the top of dry impoundment in the tailings dam.

The total concentrations of metals were determined by digesting 1 g of each sample with strong acids ($HClO_4$, HNO_3 and HF followed by HCl). The concentration of the potentially toxic elements As, Cu, Co, Cr, Fe, Mn, Mo, Ni, Pb and Zn in bulk samples and extracted solutions of the fractionation analysis were determined by ICP-OES (iCAP 6000 model) at the Central Laboratory of the Sarcheshmeh Copper Complex. Some control samples were also submitted to the Amdel Laboratory.

Mineralogical studies, including qualitative and semi-quantitative investigations of primary and secondary minerals, were implemented by X-ray diffraction (Philips Multipurpose X-ray diffraction system, MPD model) and by the Rietveld method at the Iran Mineral Processing Research Center (IMPRC). Although some of the secondary mineral phases in the sulfide mineral oxidation and AMD processes are poorly crystalline or even have amorphous structures, the Rietveld method can give semi-quantitative estimations of structural phases. In this method, if the chemical composition and mineral phases of each sample were identified, the crystalline structure of samples could be correctly refined (Dercz et al., 2008). Ore microscopy of polished sections was implemented at the Central Laboratory of Sarcheshmeh Copper Complex with a Leica DMLP Reflected/transmitted light polarizing microscope.

3.3. Chemical fractionation method

The selectivity of reagents for fractionation analysis has been a focus of criticism because a wide range of phases are associated with water–sediment systems in sulfide deposits (Hall et al., 1996; McCarty et al., 1998). Chemical fractionation analysis can be adapted to a specific mineralogy to increase the accuracy of geochemical data interpretations (Dold, 2003). After reviewing chemical fractionation schemes, especially those adapted to the specific mineralogy of porphyry Cu-sulfide ores, and evaluating the advantages and limitations of each protocol and reagents that were used for each fraction, a 9-step fractionation procedure was applied to the samples. This procedure partitions elements into nine operationally-defined geochemical fractions, as follows: water soluble, exchangeable, carbonates (acid-soluble), amorphous Fe oxyhydroxides, crystalline Fe oxides, Mn oxides, organic matter (oxidisable), primary sulfides and residuals.

To determine the fractionation pattern of potentially toxic elements, 1 g of air dried, <80 μ m solid sample was treated by successive extractions. The extracted solutions were separated from the solid phase by centrifugation at 2500 rpm for 30 min, and the supernatant was then filtered through a 0.45 μ m filter (ALBET,

Nitrato Celulosa, model), and stored at 4 °C until analysis. Each fraction was distinguished as follows:

Fraction 1 water soluble phases; 1 g of air dried solid sample was placed into 50 mL of de-ionized H_2O and shaken for 2 h at ambient temperature.

Fraction 2 exchangeable phases; by extracting the residue of fraction 1 at room temperature for 2 h by a 1 M NH₄OAc solution at pH 7, with continuous shaking.

Fraction 3 acid-soluble or carbonate phases; by extracting the residue of fraction 2 at room temperature with a 50 mL buffered acetic acid/sodium acetate solution (adjusted to pH 5 with HOAc) for 4 h, with continuous stirring. The pH was controlled during stirring, adjusting to pH 5 with HOAc.

Fraction 4 manganese oxide phases; extracted from the residue of fraction 3 with 50 mL of 0.1 M hydroxylamine hydrochloride solution prepared in 0.01 M HNO₃ (adjusted to pH 2) at ambient temperature, with continuous shaking for 30 min.

Fraction 5 amorphous Fe oxide phases; extracted from the residue of fraction 4 with 50 mL of 0.2 M NH_4 oxalate $(\text{NH}_4\text{C}_2\text{O}_4)$, adjusted to pH 3 with 0.2-M oxalic acid $(\text{H}_2\text{C}_2\text{O}_4)$, and shaken for 4 h in darkness at ambient temperature.

Fraction 6 crystalline Fe oxide phases; extracted from the residue of fraction 5 by 50 mL of 0.2 M NH₄C₂O₄, adjusted to pH 3.3 with a 0.1-M solution of ascorbic acid, at 100 °C for 30 min. Fraction 7 oxidisable phases; extracted from the residue of fraction 6 with 30% H₂O₂ (adjusted to pH 2 by use of 0.02-M HNO₃), and continuously shaken for 3 h at 85 °C.

Fraction 8 primary sulfide phases; extracted from the residue of fraction 7 with a combination of KClO₃ and HCl, followed by 4 M HNO₃ at boiling point.

Fraction 9 the residual phase; extracted from the residue of fraction 8 by digestion with HNO₃, HClO₄, HF and HCl.

All reagents were analytical grade or extra-pure quality. High purity and double de-ionized water were used for all the analyses. All standards were prepared from reagent grade chemicals. The ammonium acetate and ammonium oxalate were from BDH laboratory, Poole, England. The hydroxylamine hydrochloride and HF were from the Fluka Company, Fir Lawn (New Jersey, USA). Other reagents were from Merck, analytical grade (Darmstadt, Germany).

3.4. Precision and accuracy

The accuracy and precision of the analytical methods were verified by submitting samples to other laboratories and by submitting duplicate samples for each analytical set. The Relative Standard Deviations (RSD) for potentially toxic elements in 3 duplicated water samples were Al: 0.01%, Cd: 0.01%, Co: 0.01%, Cu: 0.02%, Fe: 0.006%, Mn: 0.01%, S: 0.006%, Ni: 0.01%, Pb: 0.35% and Zn: 0.02%. The values of As, Mo and Cr in duplicated water samples were below detection limits.

The RSD for elements in solid samples, submitted to the Amdel laboratory, Perth, Australia were <10%, ranging from 0.58% to 9.04%. The mean RSD for target elements were As: 5.32%, Co: 4.32%, Cr: 6.31%, Cu: 6.24%, Fe: 6.33%, Mn: 5.09%, Mo: 5.27%, Ni: 5.92%. Pb: 4.68% and Zn: 2.90%.

The analytical precision for each extraction step and the overall procedure was tested by subjecting five duplicate samples to the applied fractionation procedure. Also, the complete extracted solutions of three samples were submitted to the Amdel laboratory. The accuracy of the chemical fractionation method could be evaluated from the elemental recovery after whole extraction. The recovery percentage for each element in each waste sample was calculated from equation 1:

Recovery (%) =
$$[(F1 + F2 + \dots + F9)/M_{total}] \times 100$$
 (1)

where *F* is the chemical fraction and $M_{\rm total}$ is the bulk concentration of each element. The recovery percentages for target elements in each residue are presented in Table 4. Recoveries were good, averaging $104 \pm 15\%$ for As, $89 \pm 14\%$ for Co, $84 \pm 6\%$ for Cr, $93.4 \pm 9\%$ for Cu, $91 \pm 11\%$ for Fe, $91 \pm 8\%$ for Mn, $105 \pm 10\%$ for Mo, $93 \pm 6\%$ for Ni, $98 \pm 11\%$ for Pb, and $100 \pm 9\%$ for Zn.

Overall, the data indicate very good quality assurance for the extraction methods. The high RSD or recovery percentages that were observed for elements such as As and Mo, may be related to their low concentrations in some fractions, because low concentrations of any element may generally cause high relative errors (Widerlund et al., 2005; Pérez-López et al., 2008).

4. Results and discussion

4.1. Hydrochemistry

All surface effluents were considered in the water sampling strategy. Table 1 presents field parameters and concentrations of potentially toxic elements in the water samples. The pH of the samples ranges between 3.1 and 7.88 and AMD waters are predominantly associated with rock waste drainages (W5, W6, W7 and W8), reject waste drainage (W16), and the tailings pond (W20, W21 and W22). The pH of pit water, Shour River (Fig. 1) and industrial waste water are neutral to slightly acidic, while the pH of natural springs is neutral.

According to the relative concentration of major cations and anions ions using a conventional piper diagrams (Freeze and Cherry, 1979), the water samples can be classified into two main types: Ca-SO₄ and Na-SO₄. However, other water types such as Ca-HCO₃ (W2), Mg-SO₄ (W7), Na-HCO₃ (W17) and Na-SO₄ (W20 and W22) are also present (Fig. 3). In the piper diagrams distinct differences are observed between AMD water originating from mine waste rocks and the water associated with the tailings. The water of drainage from rock waste is mainly Ca-SO₄, but AMD water drainage from tailings is mainly Na-Cl and Na-SO₄.

Potentially toxic element concentrations in water samples show considerable variation. Most of these elements in natural waters (W1, W2 and W3) are below detection limits or below recommended values for drinking water (USEPA, 2009) (excluding As). On the other hand, waters affected by AMD have high values of almost all potentially toxic elements. Elevated concentrations of Al $(6020 \mu g/L)$, Cd $(207 \mu g/L)$, Co $(1310 \mu g/L)$, Cu $(7000 \mu g/L)$, Ni $(1350 \mu g/L)$, Mn $(95,800 \mu g/L)$, and Zn $(27,400 \mu g/L)$ are observed in rock waste drainage. High values of these metals are also observed in reject waste drainage (W16) and tailings pond water. The environmental and geochemical association of metals can be predicted from the correlation coefficients. The correlation coefficient matrix is listed in Table 2. In general, Cd, Co, Cu, Zn, Ni, Al, Fe, Mn and S are positively and significantly correlated and show a negative correlation with pH. The significantly positive correlation between the variables (or trace elements) may suggest a common origin and similar solubilities in waters of a given pH. The primary source of acidity during the weathering of porphyry deposits is disseminated pyrite (Verplanck et al., 2009). The negative correlation between pH and S (-0.67), pH and Fe (-0.45), and positive correlation between Fe and S (0.58) in water samples of the Sarcheshmeh porphyry Cu mine demonstrate this source.

The geochemical behavior of As and Mo in the investigated water samples is different from elements such as Cd, Co, Cu, Zn, Ni, Al and S. The maximum concentration of As is observed in industrial waste waters (W17, 442 μ g/L at pH 7.57). The As concentrations in natural spring samples (W1 and W3) with neutral pH are higher than AMD waters in the investigated samples. This

Table 1 Values of field parameters and potentially toxic element concentrations in water samples.

Sample	Location	pН	EC (uS/cm)	S/cm) TDS (mg/L)	Metals (µg/L)												ls
					ICP-N	⁄IS							ICP-OES			ICP-OES	Mohr's method
					As	Cd	Co	Cu	Mo	Ni	Pb	Zn	Al	Fe	Mn	S (mg/L)	Cl (mg/L)
W1	Natural spring	7.4	956	612	15	1.8	2.3	<2	0.6	13	0.5	72	<50	30	<50	69	24.9
W2	Natural spring	7.88	535	345	<5	< 0.2	< 0.2	<2	6.6	2	0.3	12	<50	20	<50	50	17.5
W3	Natural spring	7.85	312	200	25	< 0.2	0.4	<2	5	2	0.6	39	<50	10	<50	110	788
W4	RWD dump 25	6.63	720	460	34	57.8	212	2150	0.7	338	0.4	7056	<50	<10	27,100	122	17.8
W5	RWD dump 26	5.08	960	615	<5	59.1	116	11,700	0.8	141	0.7	3729	3050	20	14,600	133	21.3
W6	RWD dump 11	3.1	1980	1286	<5	207	517	70,000	0.3	1350	2.4	13,700	50,900	110	50,060	531	74.5
W7	RWD dump 31	3.68	2250	1440	<5	180	1310	8250	0.3	1050	12.6	27,400	60,000	740	95,800	508	146
W8	RWD dump 15	3.69	1165	745	<5	21.9	202	21,800	< 0.1	149	1.5	2400	31,200	330	90,700	227	21.3
W9	Pit mine water	6.5	655	420	6	< 0.2	0.5	<2	0.4	8	0.7	70	<50	250	380	97	10.7
W10	Mine pit water	6.7	915	585	<5	0.4	18.3	<2	17.5	12	1.0	299	<50	70	700	130	10.7
W11	Mine pit water	5.4	1210	775	<5	38.3	119	11,300	4.1	224	0.6	3060	90	930	10,000	222	10.6
W12	Mine pit water	6.62	1225	780	8	< 0.2	24.3	<2	4.7	15	3.0	316	<50	7780	1790	201	10.7
W13	Shour river	5.88	1190	760	<5	35.8	137	1940	6.3	275	1.0	3260	80	40	11,600	223	10.7
W14	Shour river	6.19	2750	1760	<5	79.3	102	9570	5.3	781	0.7	4800	<50	20	24,100	485	42.6
W15	Shour river	7.61	5655	3620	45	13.3	81.7	<2	18.5	151	2.1	294	380	150	7580	375	1290
W16	Reject waste drainage	3.16	4890	3130	<5	90.4	485	25,000	0.1	1140	0.3	6230	39,300	13,700	27,900	728	675
W17	Industrial waste water	7.57	1660	1060	442	9.9	2.1	<2	15.5	16	28.8	380	<50	280	1050	87	192
W18	Industrial waste water	6.88	5100	3265	40	25.9	154	<2	27.7	281	3.0	2120	150	60	13,700	450	1160
W19	Tailings waste water	7.92	5900	3780	6	6.2	32.6	<2	335	88	0.6	94	<50	<10	6230	594	1150
W20	Tailings waste water	4.26	4910	3141	<5	39.3	206	4670	2080	653	5.1	2760	29,200	5090	9630	748	770
W21	Tailings waste water	3.57	9100	5825	9	316	2140	149,900	1020	1740	1.4	20,300	154,000	19,300	73,700	1495	1690
W22	Tailings waste water	4.34	4795	3070	<5	20.1	94	<2	2900	240	1.1	1190	3890	80	5670	702	778
Drinking water regulations (USEPA, 2009)		6.5–8.5 ^a		500 ^c	10 ^a	5 ^a	-	1300 ^b , 1000 ^c	-	-	15 ^b	5000°	50 – 200°	300°	50 ^c	-	4 ^d

RWD: rock waste drainage.

<sup>a Maximum contaminant level.
b Treatment technique (action level).
c Secondary maximum contaminant level.
d Maximum residual disinfectant level.</sup>

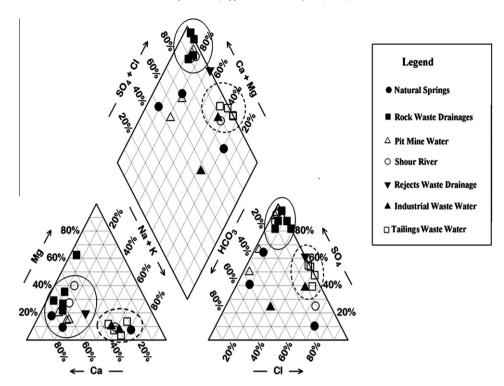


Fig. 3. Water samples plotted on a conventional piper diagram (Freeze and Cherry, 1979). The two distinct groups of water can be distinguished, based on major and minor ions.

Table 2Correlation matrix for trace elements, S, Cl and pH in water samples.

Correlation	As	Cd	Co	Cu	Mo	Ni	Pb	Zn	Al	Fe	Mn	S	Cl	pН
As	1													
Cd	-0.23	1												
Co	-0.21	0.91 ^a	1											
Cu	1 ^a	0.86^{a}	0.8^{a}	1										
Mo	-0.23	0.17	0.13	0.24	1									
Ni	-0.24^{a}	0.92^{a}	0.83^{a}	0.76^{a}	0.15	1								
Pb	-0.85	0.2	0.06	-0.12	-0.04	0.01	1							
Zn	-0.22	0.88^{a}	0.88^{a}	0.5	0.00	0.82^{a}	0.16	1						
Al	-0.99^{a}	0.91^{a}	0.95 a	0.9^{a}	0.08	0.87^{a}	0.19	0.75^{a}	1					
Fe	-0.38	0.64^{a}	0.68 a	0.72^{a}	0.18	0.64^{a}	-0.09	0.39	0.78^{a}	1				
Mn	-0.25	0.66^{a}	0.72^{a}	0.42	0.05	0.62^{a}	0.33	0.79^{a}	0.66^{a}	0.25	1			
S	-0.31	0.7^{a}	0.76^{a}	0.89^{a}	0.53 ^b	0.8^{a}	-0.09	0.55^{a}	0.83^{a}	0.75^{a}	0.38	1		
Cl	-0.15	0.25	0.4	0.77^{a}	0.39	0.32	-0.07	0.12	0.41	0.52 ^b	0.03	0.71^{a}	1	
pН	0.35	-0.64^{a}	-0.58^{a}	-0.5	-0.37	-0.74^{a}	0.06	-0.63^{a}	-0.59^{b}	-0.45^{b}	-0.67^{a}	0.58^{a}	-0.02	1

^a Correlation is significant at the 0.01 level (2-tailed).

element has low concentrations (in some cases below detection limits; <5 μ g/L) in all investigated AMD waters. The different behavior of As in mine water samples has also been shown by other authors (Marszalek and Wasik, 2000; Williams, 2001). The hydrochemical results also showed that the Mo concentrations in AMD water draining from rock waste dumps are different from the AMD water that is produced from tailings. In the first group, Mo concentrations are low (<0.8 μ g/L), while very high values of Mo (2900 μ g/L) are observed in AMD water from the tailings pond. Dzombak and Morel (1990) showed that in contrast to bivalent cations, which are mobile under acidic conditions, oxyanions like Mo(V, VI) and As(V) show increasing adsorption to Fe oxyhydroxides with decreasing pH. However, AMD samples that were collected from the tailings pond showed high values of Mo, which will be discussed later in the paper.

According to the classification based on pH and metal concentrations proposed by Ficklin et al. (1992), AMD waters that are mainly related to mining and waste processing are categorized as the "high metal" or even "extreme metal" groups (Fig. 4). Among the other water samples, only natural spring waters fall into the near neutral low metal group, and other samples can mainly be classified as part of the near neutral high metal group.

According to the results obtained from the hydrochemical investigations, it can be suggested that mining and blasting procedures have increased the volume and porosity of waste rocks, creating large pores and channels through which atmospheric gases and water could be transported; consequently, the sulfide minerals are oxidized in rock and reject wastes. It is suggested that oxidation of sulfide minerals, especially pyrite, is responsible for acid mine drainage production in rock waste dumps and reject waste

^b Correlation is significant at the 0.05 level (2-tailed).

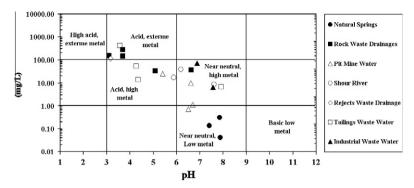


Fig. 4. Water samples plotted on the Ficklin et al., (1992) diagram based on pH and metal(loid) (Al + As + Cd + Co + Cu + Fe + Mn + Mo + Ni + Pb + Zn) concentration.

materials. On the other hand, it seems that little oxidation of sulfide minerals occurs below the water level as a result of continuous pumping of water from the Sarcheshmeh pit mine, and few metals are leached from above, resulting in a relatively non-environmentally detrimental mine water. Acid mine water rich in toxic metals will be produced if the pumps are turned off and the level of water rises in the pit (Banks et al., 1997; Gammons and Duaime, 2005).

Although the sulfide minerals, especially pyrite, are the prime sources of AMD associated with tailings in the Sarcheshmeh mine, the current AMD production is directly related to secondary minerals. Several authors have reported that prolonged precipitation of secondary minerals may occur at the surface or at a particular depth of tailings and waste rock piles (McSweeney and Madison, 1988; Holmström and Ohlander, 1999). A layer of secondary minerals is formed at the top of the dry impoundments of the Sarcheshmeh dammed tailings pond (Fig. 3E). These secondary minerals are formed in response to a combination processes, such as oxidation of sulfide minerals, capillary force, evaporation, hydrolysis and neutralization (Lottermoser, 2003). The volume of the Sarcheshmeh tailings pond increased after its development project and new tailings were directly discharged over the old dry impoundments. The dissolution of secondary minerals, especially highly soluble acid salts formed at the top of the dry impoundment, resulted in very acidic water in a very short period of time. This AMD water is highly polluted by metals and other water constituents, especially SO_4^{2-} and Cl^- ions.

The AMD water samples clearly demonstrate that these polluted waters are derived from different sources and contain different concentrations of major and minor ions. High values of SO_4^{2-} , Cl⁻ and Na⁺ in AMD water of the Sarcheshmeh tailings pond are associated with the dissolution of the evaporative layer of secondary minerals formed at the top of dry impoundments. According to the classification of water samples (Fig. 4), the dissolved metal content of acidic waters will decrease with increasing pH; however despite pH changes, such waters are still of environmental concern because the elements can remain in solution. For example water samples such as mine pit waters (W10 and W11), in spite of pH values near neutral, were categorized as "neutral high metal" group. These conditions have also been reported by some authors in mines (Carroll et al., 1998; Plumlee et al., 1999) and even for the surface waters from unmined areas (Plaza-Toledo, 2005). For example, Plaza-Toledo (2005) found that surface waters downstream from unmined porphyry Cu deposits in the Cordillera Central of Puerto Rico reached maximum dissolved concentrations of 110 mg/L SO₄, 0.56 mg/L Al, 0.13 mg/L Cu, 15.9 mg/L Fe and 0.04 mg/L Zn, while the pH was high (7.7-8.6).

4.2. Mineralogy

A great variety of primary and secondary mineral phases were identified in the waste samples associated with the Sarcheshmeh

Cu mine. Table 3 represents semi-quantitative mineralogical compositions of wastes. Because of the presence of high contents of amorphous structures, the total mineral compositions do not total 100% in some samples, such as S3 and S9. Quartz is the main primary mineral found in almost all samples. The most abundant clay minerals are sericite, chlorite and vermiculite. Albite and orthoclase are other primary non-sulfide minerals that are found in some samples. High contents of primary sulfide minerals, including chalcopyrite (FeCuS₂), molybdenite (MoS₂) and pyrite (FeS₂), were found in sediments associated with waste water effluents from the concentration plants. The volume of these waste waters is negligible compared to other processing wastes, such as tailings and their discharge is minimal. Ore microscopy studies of polished sections show that other sulfide minerals such as chalcocite (Cu₂S) and covellite (CuS) are also present in contaminated effluents of the concentration plant (Fig. 5A). High values of Cu (98,200 mg kg⁻¹), Fe $(117,000 \text{ mg kg}^{-1})$, Mo $(1950 \text{ mg kg}^{-1})$, as well as As (896) $mg kg^{-1}$), Pb (1490 $mg kg^{-1}$), Zn (2570 $mg kg^{-1}$), Cd (17.0 $mg kg^{-1}$), Bi $(17.4 \text{ mg kg}^{-1})$ and Sb (152 mg kg^{-1}) , in these wastes are related to the presence of primary ore minerals, because some of the sulfide minerals like pyrite and chalcopyrite may contain high values of minor and trace element constituents in the form of cation substitutions (Vaughan and Craig, 1978). Pyrite is the main primary sulfide mineral in sub-surface tailings samples and comprises 7-8% of the tailings mineralogical compositions (Fig. 5B).

The most important secondary mineral phases in the investigated waste samples that were identified by XRD analysis are: alunite [KAl $_3$ (SO $_4$) $_2$ (OH) $_6$], gypsum [CaSO $_4$ ·2H $_2$ O], magnesiocopiapite [MgFe $_2$ * 3 (SO $_4$) $_6$ (OH) $_2$ ·20H $_2$ O], hydronium jarosite [(H $_3$ O)Fe* 3 $_3$ (SO $_4$) $_2$ (OH) $_6$], kornelite [Fe* 3 $_2$ (SO $_4$) $_3$ ·7–8H $_2$ O], coquimbite [Fe* 3 $_2$ (SO $_4$) $_3$ ·9H $_2$ O], plancheite [CuSSi $_8$ O $_2$ 2(OH) $_4$ ·H $_2$ O], eriochalcite [CuCl $_2$ ·2H $_2$ O], palygorskite [(Mg,Al) $_2$ Si $_4$ O $_1$ 0(OH)·4H $_2$ O] and bonattite [CuSO $_4$ ·3H $_2$ O]. Notably, it is the first time that these secondary mineral phases have been reported in the Sarcheshmeh porphyry Cu mine.

Gypsum was found in nearly all investigated waste environments, including rock waste drainage, weathered reject wastes and in the evaporation layer of tailings. This mineral comprises about 91% of the mineralogical composition of some secondary sediment phases associated with rock waste drainage (Fig. 6A). Gypsum can be formed as a result of an increase in Ca and SO₄ concentration or neutralization of AMD waters. It seems that the Ca required for gypsum formation is released by acid weathering of silicate minerals and calcite that were reported by Shahabpour and Doorandish (2007) in the feldspar porphyry and biotite porphyry dykes, pebble dykes and trachyandesite volcanic wall rocks of the Sarcheshmeh mine. The carbonate rock units (Calcareous terraces unit in Fig. 1) are not present in the AMD catchments of the Sarcheshmeh Cu mine and do not have any role in buffering reactions of the surface AMD waters and providing the Ca required for gypsum formation.

 Table 3

 Semi-quantitative mineralogical composition of wastes and efflorescence salts associated with rock waste drainage, weathered reject wastes, tailings and waste associated with the concentration plants.

Sample	Mineral composition (%)																		
	Qtz	Ab	Ser	Chl	Vrm	Or	Сср	Ру	Mo	Gp	Alu	Kor	Pln	Mg-Cp	Cq	Hyd-Jt	Erc	Bn	Plg
S1	5	-	_	_	-	-	_	_	_	91	4	_	_	-	-	_	_	_	_
S2	35	18	20	_	4	-	_	_	_	6	_	9	8	_	_	_	_	_	_
S3	32	_	10	7	5	-	_	_	_	14	_	_	_	15	8	9	_	_	_
S4	30	_	21	8	-	-	27	13	1		_	_	_	_	_	_	_	_	_
S5	28	5	8		6	-	_	_	_	39	_	_	_	_	_	14	_	_	_
S6	49	-	22	12	-	10	-	7	-	-	-	-	-	_	-	-	-	-	-
S7	40	7	26	13	_	6	_	8	-	-	_	-	_	_	-	_	_	-	_
S8	15	_	-	_	-	-	-	-	-	13	_	-	-	-	-	-	16	9	16
S9	39	11	25	9	-	9	-	-	-	-	_	-	-	-	-	-	-	-	-

Abbreviations: Qtz: quartz, Ab: Albite, Ser: Sericite, Chl: Chlorite, Vrm: Vermiculite, Or: Orthoclase, Ccp: Chalcopyrite, Py: Pyrite, Mo: Molybdenite, Gp: Gypsum, Alu: Alunite, Kor: Kornelite, Pln: Plancheite, Mg-Cp: Magnesiocopiapite, Cq: Coquimbite, Hyd-Jt: Hydronium Jarosite, Erc: Eriochalcite, Bn: Bonattite, Plg: Palygorskite. Sample descriptions: S1: Rock waste drainage of dump 26, S2: Rock waste drainage of dump 25, S3: Rock waste drainage of dump 15, S4: waste associated with concentration plant, S5: Old weathered rejects waste, S6 & S7: Sub-surface tailings waste, S8: Surface tailings waste (secondary mineral crust), S9: Surface tailings waste.

A variety of secondary Fe minerals were identified in efflorescence sediments associated with rock waste drainages. Magnesiocopiapite, hydronium jarosite, kornelite, and coquimbite are the most important Fe-sulfate minerals found in rock waste drainage of the Sarcheshmeh Cu mine. These secondary minerals can store $\mathrm{Fe^{+3}}$, $\mathrm{SO_4^{2-}}$, and potentially hazardous elements such as As, Cd, Cu and Zn, as well as acidity and Fe²⁺ (an oxidant) during the dry seasons, and can release them during the wet seasons (Lin, 1997). Magnesiocopiapite comprises 15% of the mineral composition of efflorescence salts associated with drainage of dump 15. Kornelite and coquimbite comprise 7% and 8% of the mineralogical composition of efflorescence salts associated with dumps 25 and 15, respectively. These minerals as the simple hydrous metal sulfate with trivalent metal cations have been reported from several localities that are mostly related to former mining sites (Joeckel et al., 2005; Qin et al., 2008).

From the alunite-jarosite group minerals, alunite was found in the drainage of dump 26. Hydronium jarosite also comprises 9% of the mineralogical composition of efflorescent Fe sulfates of dump 15 and 14% of weathered reject wastes.

Plancheite, eriochalcite and bonattite are the most important secondary Cu minerals in the investigated waste samples of the Sarcheshmeh mine. Plancheite is a rare secondary Cu silicate that has a distinctive blue color (Evans and Mrose, 1997). This mineral was found in drainage of Dump 25. Eriochalcite and bonattite, found in the evaporative surface layer of tailings, comprise 12.6% and 19% of the mineralogical composition of evaporative phases, respectively. About 30% of the mineralogical composition of the tailings crust layer has an amorphous structure, rendering impossible their detection by XRD analysis.

The generation of highly contaminated effluents and development of new supergene secondary minerals are the two main results of mineral-water interaction in waste rocks associated with the Sarcheshmeh porphyry Cu mine. Formation of the secondary minerals in arid and semi-arid climates such as the Sarcheshmeh area is generally a response to evaporation and neutralization processes. A significant fraction of metals released by sulfide oxidation in wastes can be precipitated as secondary minerals (Lin, 1997; Lin and Herbert, 1997) or adsorbed by these phases (Rose and Ghazi, 1998). Thus, the mineralogy of secondary mineral phases is important for assessing metal release, retention and transport from highmetal sulfide wastes. The highly acidic waters associated with rock dumps, reject wastes and surface-weathered tailings are usually supersaturated in secondary minerals that precipitate and sequestrate relatively high concentrations of potentially toxic elements from solution. The saturation indices for secondary minerals have been given by several authors (e.g. Sidenko and Sherriff, 2005;

España et al., 2008). The type of secondary minerals formed in mine waste is primarily controlled by the composition of the wastes. Metalliferous waste rocks tend to contain abundant secondary metal sulfate salts (Lottermoser, 2003).

The alunite-jarosite mineral group consists of Fe and Al hydroxy sulfate minerals and is less soluble than the efflorescent sulfate salts (Nordstrom, 1982; Lapakko, 2002). If the pore water pH decreases (pH < 3) and high sulfate concentrations are present, jarosite and hydronium jarosite will precipitate (McGregor and Blowes, 2002). Such conditions are compatible with precipitation of hydronium jarosite in mining waste drainage and weathered reject wastes of the Sarcheshmeh porphyry Cu mine.

Among the secondary minerals distinguished, Fe precipitates can play one of the most important roles in AMD water quality. They control not only the Fe and SO₄ concentrations, but also the concentration of other pollutants (Balistrieri et al., 2007). These Fe precipitates also have an important role in the amount of acidity that might be developed from sulfide waste environments (Dold and Fontboté, 2001). The mineralogy of secondary Fe precipitates is complex and depends on the solution composition, pH, temperature, redox conditions and the rate of Fe²⁺ oxidation (Alpers et al., 1994; Cravotta, 1994). These secondary minerals, such as the copiapite-group, occur as efflorescence salts near acidic or even extremely acidic drainages (Nordstrom and Alpers, 1999b) and are relatively common Fe-sulfate minerals in oxidized sulfide deposits and waste environments (Jambor et al., 2000; Nordstrom, 1982).

As noted in Section 4.1, the quality of water in the Sarcheshmeh tailings pond can become highly acidic due to discharge of new tailings over the old dry impoundments. It is clear that dissolution of soluble secondary mineral phases that are formed at the top of the dry impoundment is responsible for the development of highly contaminated waters over short periods of time. For example, the very high concentrations of Cl (1690 mg kg⁻¹) and Cu (150 mg kg⁻¹) in tailings pond waters are related to eriochalcite dissolution, because this mineral is very soluble, and about 77.6% of its chemical composition made up of Cu and Cl (36.89% and 40.68%, respectively) (Roberts et al., 1990). Positive correlations between Cl, Cu and S in water samples also are consistent with eriochalcite and other secondary mineral dissolution in dry impoundments of the tailings dam.

4.3. Chemical fractionation

The extractable concentrations of As, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn of mine and processing wastes in each fraction are shown in Table 4. The total concentration and recovery values of target elements in samples are also shown in this table. The extracted

 Table 4

 Results obtained from 9 operationally defined chemical fractionation methods: F1(water soluble fraction), F2 (Exchangeable fraction), F3 (acid-soluble fraction), F4 (manganese oxides fraction), F5 (amorphous Fe oxides fraction), F6 (Crystalline Fe oxide Fraction), F7: (Oxidisable fraction), F8 (Primary sulfide fraction), F9 (Residual fraction).

Sample	Fraction	Elements (mg kg ⁻¹) and Recovery values (%)										
		As	Co	Cr	Cu	Mn	Mo	Ni	Pb	Zn		
S1	F1	0.43	20.0	BDL	4210	50.1	5240	bdl	39.0	BDL	154	
Rock waste drainage of dump 26	F2	1.01	2.97	BDL	1320	16.5	532	0.62	8.42	BDL	65.4	
	F3	5.03	2.02	4.67	3910	942	61.2	0.58	5.97	34.1	205	
	F4	2.72	0.35	0.99	377	285	23.6	0.25	2.51	7.78	24.0	
	F5	22.9	0.28	1.37	789	1240	24.4	3.56	4.49	17.1	23.8	
	F6	2.80	0.47	0.22	63.9	1170	43.4	0.78	0.73	3.43	18.	
	F7	3.21	0.50	0.16	226	568	23.9	6.01	0.67	1.06	78.	
	F8	1.26	0.33	0.25	31.9	1070	32.7	0.25	0.58	4.03	30.	
	F9	1.18	0.42	2.22	22.6	919	11.6	3.37	1.71	4.42	7.9	
	Sum	40.5	27.35	9.87	10,950	6261	5993	15.42	64.09	71.9	199	
	Bulk	40.0	33.0	11.0 89.7	11,700	5880 106.5	6770	14.0	62.0	65.0	186 107	
S2	Recovery (%) F1	101.3 0.58	82.9 1.54	0.16	93.6 30.8	106.5 31.5	88.5 782	110.1 BDL	103.4 2.59	110.6 BDL	146	
Rock waste drainage of dump 25	F2	1.45	12.8	0.10	12,400	16.0	1610	BDL	15.3	1.10	179	
Rock waste drainage of dump 25	F3	10.4	15.4	1.27	41,600	415	665	BDL	89.6	14.15	672	
	F4	0.75	18.1	0.14	4360	323	847	BDL	14.3	0.65	647	
	F5	29.8	14.3	0.63	5839	1010	356	0.75	38.3	8.36	762	
	F6	19.1	0.53	1.14	41.0	5620	69.3	2.96	2.87	4.15	14.	
	F7	0.00	0.58	0.35	1110	188	22.5	1.70	2.17	0.68	86.	
	F8	8.08	2.27	4.08	385	12,300	88.1	3.96	4.95	82.26	123	
	F9	1.23	0.33	4.31	36.1	1970	19.5	0.99	1.48	4.50	25.	
	Sum	71.38	65.7	12.48	65,850	21,870	4459	10.36	171.6	115.9	10,	
	Bulk	52.9	57.6	17.0	65,100	27,000	4840.0	9.4	172.0	147	94	
	Recovery (%)	134.9	114.1	73.4	101.2	81.0	92.1	110.2	99.8	78.8	109	
3	F1	42.1	82.3	13.3	13,400	32,900	1970	3.20	58.6	BDL	78	
Rock waste drainage of dump 15	F2	1.29	2.77	0.08	299	215	70.7	0.18	2.17	BDL	19.	
	F3	1.50	0.33	0.18	93.9	416	3.54	BDL	0.26	1.82	10.	
	F4	0.07	0.03	0.07	9.77	136	0.48	BDL	0.02	BDL	5.5	
	F5	22.8	0.36	0.26	144	8450	9.08	12.4	0.16	40.6	9.6	
	F6	3.25	0.13	0.57	BDL	1970	12.3	1.56	0.21	23.0	0.4	
	F7	1.41	1.91	0.05	4200	2410	3.48	6.38	1.53	BDL	51.	
	F8	81.8	4.03	1.54	1480	10,900	12.8	416	4.18	21.1	15	
	F9	2.41	0.67	1.53	60.0	822	5.36	30.00	1.79	3.97	7.2	
	Sum	156.6	92.53	17.58	19,690	58,220	2090	469.7	68.94	90.49	10	
	Bulk	183	127	20.4	26,400	60,100	2550	528	80.4	99.9	110	
	Recovery (%)	85.6	72.9	86.2	74.6	96.9	82.0	88.9	85.7	90.5	90.	
54	F1	0.06	BDL	0.05	2.55	1.45	0.16	2.30	0.05	0.29	0.4	
Sediments associated with concentration plant effluents	F2	5.57	0.37	0.03	4210	BDL	20.5	5.25	1.28	3.02	57.	
	F3	58.8	0.82	0.94	1310	1840	88.8	0.50	1.82	185	97.	
	F4	2.83	0.13	0.10	0.12	252	17.7	0.00	0.39	4.85	15.	
	F5	55.9	1.13	2.32	2480	2830	84.8	2.27	1.90	6.37	37.	
	F6	6.83	0.76	0.75	BDL	2066	85.4	0.76	1.38	2.99	6.9	
	F7	0.09	6.68	0.05	26,500	1380	32.4	BDL	8.70	44.2	854	
	F8	820	22.5	1.49	60,600	99,600	27.9	1890	26.8	980	16	
	F9	30.1	1.85	3.84	3570	3930	8.99	140	6.60	31.8	73.	
	Sum	980.2	34.23	9.57	98,670	111,900	366.7	2041	48.9	1259	27	
	Bulk	896	36.5	10.6	98,200	117,000	425	1950	49.5	1490	25	
	Recovery (%)	109.4	93.8	90.3	100.5	95.6	86.3	104.7	98.8	84.5	10	
55	F1	0.07	4.04	0.06	837	59.4	75.0	BDL	2.95	BDL	51.	
Neathered rejects waste	F2	0.38	0.05	0.01	32.4	0.39	1.58	BDL	0.10	BDL	1.7	
	F3	0.92	0.12	0.19	212	199	1.12	BDL	0.21	1.14	6.1	
	F4	0.06	0.03	0.03	14.7	162	1.89	BDL	0.02	0.34	6.2	
	F5	52.6	0.22	7.94	501	48,700	6.53	11.4	0.52	29.7	13.	
	F6	82.2	0.17	4.22	7.26	1790	8.72	13.9	0.26	16.2	9.5	
	F7	BDL	0.69	0.37	893	2880	7.47	BDL	0.99	2.55	25	
	F8	25.5	4.73	3.93	514	37,000	51.0	29.2	6.64	76.7	85	
	F9	4.18	2.72	7.89	63.7	2390	16.0	35.1	3.70	11.6	40.	
	Sum	165.9	12.77	24.62	3075	93,180	169.3	89.6	15.39	138.2	24	
		201 82.5	12.4	29.3	3300	88,000	185	103	16.9	134	28	
	Bulk		103.0	84.0	93.2 0.43	105.9	91.5	87,0	91.1	103.1	84.	
c	Recovery (%)		DDI		11/13	BDL	1.37	9.91	0.03	BDL	0.8 9.0	
	Recovery (%) F1	0.04	BDL	0.01		DDI	100	2 10	0.50	DDI	นก	
	Recovery (%) F1 F2	0.04 0.95	0.30	0.01	90.2	BDL	19.9	2.10	0.59	BDL		
	Recovery (%) F1 F2 F3	0.04 0.95 2.86	0.30 1.31	0.01 0.51	90.2 141	629	39.9	0.31	1.51	8.28	32.	
	Recovery (%) F1 F2 F3 F4	0.04 0.95 2.86 0.12	0.30 1.31 0.26	0.01 0.51 0.13	90.2 141 7.58	629 304	39.9 10.0	0.31 0.10	1.51 0.32	8.28 0.57	32. 8.7	
	Recovery (%) F1 F2 F3 F4 F5	0.04 0.95 2.86 0.12 4.97	0.30 1.31 0.26 2.72	0.01 0.51 0.13 8.96	90.2 141 7.58 58.7	629 304 5910	39.9 10.0 220	0.31 0.10 9.92	1.51 0.32 3.04	8.28 0.57 7.12	32. 8.7 45.	
	Recovery (%) F1 F2 F3 F4 F5 F6	0.04 0.95 2.86 0.12 4.97 0.74	0.30 1.31 0.26 2.72 0.44	0.01 0.51 0.13 8.96 3.53	90.2 141 7.58 58.7 0.09	629 304 5910 741	39.9 10.0 220 61.0	0.31 0.10 9.92 0.86	1.51 0.32 3.04 0.69	8.28 0.57 7.12 1.98	32. 8.7 45. 2.4	
	Recovery (%) F1 F2 F3 F4 F5 F6 F7	0.04 0.95 2.86 0.12 4.97 0.74 1.47	0.30 1.31 0.26 2.72 0.44 11.5	0.01 0.51 0.13 8.96 3.53 0.33	90.2 141 7.58 58.7 0.09 705	629 304 5910 741 9500	39.9 10.0 220 61.0 71.9	0.31 0.10 9.92 0.86 35.4	1.51 0.32 3.04 0.69 7.85	8.28 0.57 7.12 1.98 11.4	32. 8.7 45. 2.4 51.	
	Recovery (%) F1 F2 F3 F4 F5 F6 F7 F8	0.04 0.95 2.86 0.12 4.97 0.74 1.47 4.93	0.30 1.31 0.26 2.72 0.44 11.5 5.24	0.01 0.51 0.13 8.96 3.53 0.33 28.9	90.2 141 7.58 58.7 0.09 705 67.3	629 304 5910 741 9500 13,500	39.9 10.0 220 61.0 71.9 95.2	0.31 0.10 9.92 0.86 35.4 30.2	1.51 0.32 3.04 0.69 7.85 24.9	8.28 0.57 7.12 1.98 11.4 19.9	32. 8.7 45. 2.4 51. 29.	
	Recovery (%) F1 F2 F3 F4 F5 F6 F7 F8 F9	0.04 0.95 2.86 0.12 4.97 0.74 1.47 4.93 0.63	0.30 1.31 0.26 2.72 0.44 11.5 5.24 0.40	0.01 0.51 0.13 8.96 3.53 0.33 28.9 13.0	90.2 141 7.58 58.7 0.09 705 67.3 11.0	629 304 5910 741 9500 13,500 1480	39.9 10.0 220 61.0 71.9 95.2 7.31	0.31 0.10 9.92 0.86 35.4 30.2 2.33	1.51 0.32 3.04 0.69 7.85 24.9 2.33	8.28 0.57 7.12 1.98 11.4 19.9 1.46	32. 8.7 45. 2.4 51. 29. 8.3	
	Recovery (%) F1 F2 F3 F4 F5 F6 F7 F8 F9 Sum	0.04 0.95 2.86 0.12 4.97 0.74 1.47 4.93 0.63 16.71	0.30 1.31 0.26 2.72 0.44 11.5 5.24 0.40 22.15	0.01 0.51 0.13 8.96 3.53 0.33 28.9 13.0 54.39	90.2 141 7.58 58.7 0.09 705 67.3 11.0	629 304 5910 741 9500 13,500 1480 32,060	39.9 10.0 220 61.0 71.9 95.2 7.31 526.6	0.31 0.10 9.92 0.86 35.4 30.2 2.33 91.13	1.51 0.32 3.04 0.69 7.85 24.9 2.33 41.26	8.28 0.57 7.12 1.98 11.4 19.9 1.46 50.71	32. 8.7 45. 2.4 51. 29. 8.3	
S6 Sub-surface tailings waste	Recovery (%) F1 F2 F3 F4 F5 F6 F7 F8 F9	0.04 0.95 2.86 0.12 4.97 0.74 1.47 4.93 0.63	0.30 1.31 0.26 2.72 0.44 11.5 5.24 0.40	0.01 0.51 0.13 8.96 3.53 0.33 28.9 13.0	90.2 141 7.58 58.7 0.09 705 67.3 11.0	629 304 5910 741 9500 13,500 1480	39.9 10.0 220 61.0 71.9 95.2 7.31	0.31 0.10 9.92 0.86 35.4 30.2 2.33	1.51 0.32 3.04 0.69 7.85 24.9 2.33	8.28 0.57 7.12 1.98 11.4 19.9 1.46	32. 8.7 45. 2.4 51. 29. 8.3 188 192 98.	

(continued on next page)

Table 4 (continued)

Sample	Fraction	Elements (mg kg ⁻¹) and Recovery values (%)										
		As	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Zn	
S7	F1	0.24	0.01	BDL	1.90	BDL	1.14	11.1	0.04	BDL	0.02	
Sub-surface tailings waste	F2	1.04	0.32	0.01	94.7	BDL	14.3	3.17	0.43	BDL	10.4	
-	F3	2.73	1.20	0.22	143	464	39.0	0.67	1.08	6.33	26.6	
	F4	1.76	0.89	1.03	80.4	936	51.8	0.41	1.06	3.28	17.8	
	F5	2.42	3.18	7.05	31.2	5830	423	6.24	4.91	6.32	64.3	
	F6	0.61	0.45	4.21	0.00	1080	91.5	0.61	0.60	2.47	4.55	
	F7	2.12	10.0	0.26	690	8310	95.0	43.2	9.05	8.82	67.2	
	F8	8.44	7.57	11.6	86.9	12,600	59.6	49.5	12.3	20.2	41.0	
	F9	0.66	0.36	7.28	7.16	1220	7.59	2.94	1.98	1.98	7.13	
	Sum	20.03	24.00	31.66	1135	30,440	782.9	117.8	31.44	49.40	239.	
	Bulk	20.4	29.4	38.0	1280	37,300	797	111	35.0	43.1	228	
	Recovery (%)	98.2	81.6	83.3	88.7	81.6	98.2	106.1	89.8	114.6	104.	
S8	F1	0.49	272	16.2	31,400	1730	12,900	BDL	293	BDL	3900	
Surface tailings waste (secondary mineral crust)	F2	0.44	17.4	0.36	1510	40.4	650	0.10	18.9	BDL	134	
	F3	3.50	1.11	5.57	371	2040	26.4	0.21	1.42	0.98	42.1	
	F4	0.56	0.42	1.37	83.4	1220	72.6	0.03	0.99	3.12	11.8	
	F5	7.58	0.94	16.9	254	8970	63.5	3.72	2.58	12.9	12.6	
	F6	1.42	0.59	1.20	2.60	946	21.6	0.28	0.94	0.94	5.04	
	F7	0.11	1.28	0.25	24.6	777	10.5	4.78	0.96	0.67	12.6	
	F8	1.15	1.86	2.41	24.0	6280	70.3	1.88	1.83	7.12	12.3	
	F9	0.83	0.67	2.66	32.6	2200	40.9	1.96	1.00	1.36	6.35	
	Sum	16.07	296.3	46.9	33,700	24,200	13,860	12.97	321.6	27.1	4137	
	Bulk	13.9	367	55.0	33,100	29,800	13,100	10.9	348	28.0	3830	
	Recovery (%)	115.6	80.7	85.3	101.8	81.2	105.8	119.0	92.4	96.7	108.	
\$9	F1	0.14	55.7	3.25	12,000	6.58	3970	BDL	58.5	BDL	2200	
Surface tailings waste	F2	0.96	2.76	0.08	684	0.00	211	2.60	3.34	BDL	87.3	
	F3	1.99	0.33	0.60	180	133	11.2	0.38	0.43	BDL	28.5	
	F4	0.07	0.22	0.40	20.6	267	21.6	0.01	0.41	0.13	10.5	
	F5	12.7	1.47	7.01	543	6690	115	38.6	1.80	8.48	18.3	
	F6	2.54	0.42	1.32	0.12	1820	39.4	4.50	0.59	2.21	0.87	
	F7	0.16	4.39	0.19	205	4830	11.5	28.2	2.52	4.15	15.0	
	F8	2.18	3.61	6.34	26.3	8280	44.5	34.1	4.12	28.3	23.5	
	F9	0.43	0.33	4.32	9.92	1070	8.29	4.61	1.33	4.05	5.04	
	Sum	21.20	69.2	23.5	13,670	23,100	4483	113.0	73.03	47.3	2389	
	Bulk	18.8	76.2	27.00	14,700	26,600	5110	100.	82.00	46.6	2580	
	Recovery (%)	112.8	90.8	87.1	93.0	86.8	87.7	113.0	89.4	101.5	92.6	

BDL: Below detection limit.

percentage values of metals with respect to the sum of the nine fractions are presented in Fig. 7.

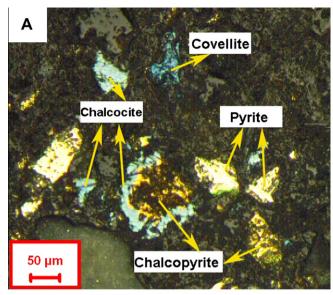
4.3.1. Efflorescence of rock waste drainage

High total values of Cu (26,400 mg kg $^{-1}$), As (220 mg kg $^{-1}$), Fe (60,100 mg kg $^{-1}$), Mn (6770 mg kg $^{-1}$), Mo (528 mg kg $^{-1}$), Pb (192 mg kg $^{-1}$), and Zn (9410 mg kg $^{-1}$) were measured in efflorescence samples associated with rock waste drainage. The fractionation patterns of these metals, especially in the water soluble fraction, are different among sediments and efflorescence salts. About 73.1% of Co (20 mg kg $^{-1}$), 38.5% of Cu (4210 mg kg $^{-1}$), 87.4% of Mn (5240 mg kg $^{-1}$), 60.9% of Ni (39 mg kg $^{-1}$), and 77.3% of Zn (1540 mg kg $^{-1}$) and only 0.8% of Fe (50.1 mg kg $^{-1}$) in efflorescence salts related to drainage of dump 26 (Fig. 7A) were released during the first step (water soluble) of the fractionation procedure, and the pH of the de-ionized water decreased to about 4. As noted in the mineralogical studies, gypsum was identified as the main water soluble mineral phase, comprising 91% of the mineral composition of this sample.

High values of elements were also released from the efflorescence salts related to dump 15 in the first step of fractionation. In this step the pH of the water decreased to 2.28% and 88.9% of Co (82.3 $\rm mg\,kg^{-1}$), 75.3% of Cr (13.3 $\rm mg\,kg^{-1}$), 68.1% of Cu (13,400 $\rm mg\,kg^{-1}$), 94.4% of Mn (1970 $\rm mg\,kg^{-1}$), 85.0% of Ni (58.6 $\rm mg\,kg^{-1}$), 56.5% of Fe (32,900 $\rm mg\,kg^{-1}$), 74.9% of Zn (783 $\rm mg\,kg^{-1}$), and 28.9% of As (42.1 $\rm mg\,kg^{-1}$) were released into the water (Fig. 7C). In particular, the dissolution of secondary Fe-sulfate minerals like magnesiocopiapite, coquimbite and hydronium

jarosite is responsible for the release of high values of metals, metalloids and H⁺ into the water, because these minerals comprise about 32% of the mineralogical composition of this sample.

Geochemical investigations show that As (220 mg kg^{-1}) , Pb (192 mg kg^{-1}) and Mo (529 mg kg^{-1}) are more concentrated in sediment and efflorescence salt phases associated with rock waste drainage. Chemical fractionation analyses show that As, Pb and Mo are dominantly associated with amorphous Fe oxides, crystalline Fe oxides and carbonates. As noted in Section 4.2, the AMD waters associated with rock waste drainage have low concentrations of Mo and Pb, and the concentration of As was below detection limits in nearly all AMD sources. Also, mineralogical studies show that secondary Fe minerals like kornelite, magnesiocopiapite, coquimbite and hydronium jarosite are abundant in rock waste drainage, and can exert important controls on the behavior of As, Mo and Pb in the water-sediment systems. Elements such as As and Mo have stable anionic species (HMoO₄⁻, H₂AsO₄⁻) under acidic and oxidizing conditions, and are generally less mobile due to absorption by secondary minerals (Dold and Fontboté, 2001). Mobility of As in mining areas with oxidizing conditions and pH values greater than 3 is restricted by Fe oxyhydroxides. Under these conditions, dissolved As species are adsorbed onto and precipitated with Fe oxyhydroxides (Marszalek and Wasik, 2000; Williams, 2001). This process is an efficient removal mechanism of As from AMD mine waters (Foster et al., 1998; Roddick-Lanzilotta et al., 2002). For example, it has been demonstrated that secondary minerals like scorodite (hydrated Fe arsenate) (Triantafyllidis and Skarpelis, 2005) and jarosite (Courtin-Nomade et al., 2003) can effectively adsorb As



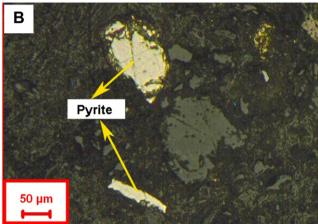


Fig. 5. Photomicrograph in plain reflected light showing the presence of primary sulfides in wastes associated with the concentration process (A) and sub-surface tailings (B).

from contaminated water. Arsenic can also substitute for SO_4^{2-} in jarosite and gypsum, and carbonate in calcite (Scott, 1987; Foster et al., 1998; Savage et al., 2000). Also, it has been reported that Pb is mainly co-precipitated with jarosite group minerals (Dold and Fontboté, 2001).

It is notable that other chemical fractions, such as the exchangeable fraction and Mn oxides, also adsorb part of the toxic elements load of rock waste drainage, although the concentrations of metals that are accompanied with these phases are far lower than the water soluble, carbonate, amorphous and crystalline Fe oxide fractions.

4.3.2. Waste effluents from concentration plants

Mineral composition also has an important control on the chemical fractionation patterns of potentially toxic elements in processing wastes. Mineralogical investigations based on XRD analysis and ore microscopy showed that primary minerals, such as chalcopyrite, pyrite, chalcocite, covellite and molybdenite, are abundant in the sediments associated with waste water effluent of the concentration plant. Chemical fractionation analyses are also consistent with the mineralogical studies. Most of the potentially toxic elements are associated with primary sulfide and oxidizing fractions in these wastes (Fig. 7D). For example, 83.7% of As, 65.7% of Co, 61.4% of Cu, 95.7% of Mo, 54.8% of Ni, 77.9% of Pb,

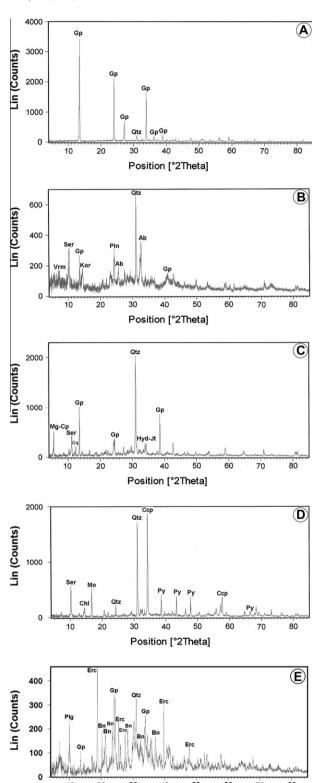


Fig. 6. Representative X-ray powder diffraction patterns of some selected waste and efflorescence salts in Sarcheshmeh Cu mine. Sample descriptions: (A) Rock waste drainage of dump 26, (B) Rock waste drainage of dump 25, (C) Rock waste drainage of dump 15, (D) Sediments associated with the waste waters of concentration plants, (E) Secondary mineral crust of tailings. Qtz: quartz, Ab: Albite, Ser: Sericite, Chl: Chlorite, Vrm: Vermiculite, Ccp: Chalcopyrite, Py: Pyrite, Mo: Molybdenite, Gp: Gypsum, Kor: Kornelite, Pln: Plancheite, Mg-Cp: Magnesiocopiapite, Cq: Coquimbite, Hyd-Jt: Hydronium Jarosite, Erc: Eriochalcite, Bon: Bonattite, Plg: Palygorskite.

Position [°2Theta]

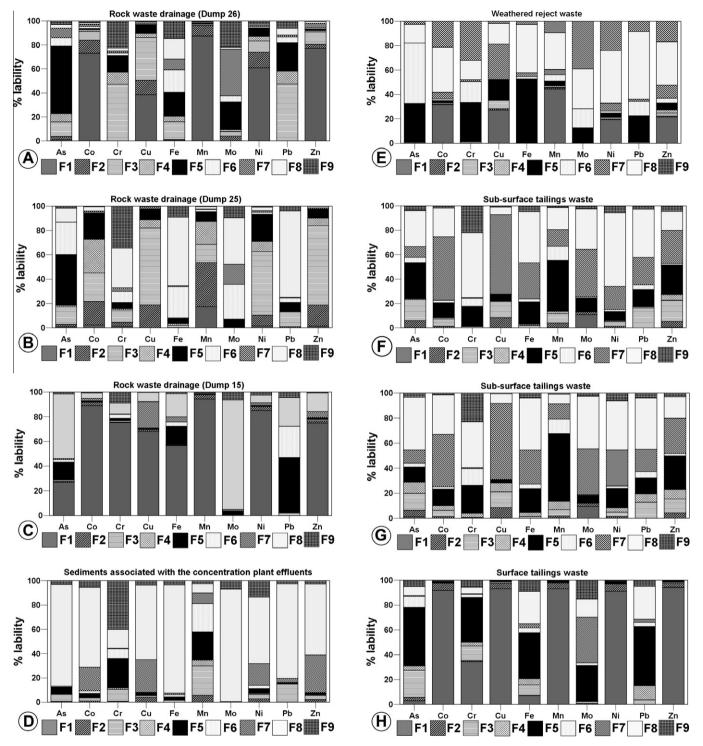


Fig. 7. Percentage of As, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb and Zn extracted in each step of the chemical fractionation procedure.

and 58.4% of Zn are in primary sulfides. In spite of very high values of As (896 mg kg $^{-1}$), Cu (117,000 mg kg $^{-1}$), Mo (1950 mg kg $^{-1}$), Pb (1490 mg kg $^{-1}$), and Zn (2570 mg kg $^{-1}$) the bioavailable or water soluble fraction in sediments associated with contaminant effluents of concentration plants are lower than efflorescence salts associated with rock waste drainage. These wastes, from an environmental point of view, must be considered a major source of pollution over long time periods, because as a result of oxidizing conditions they have potential to release AMD waters containing high concentrations of metals, metalloids and SO $_4$ into the environment.

4.3.3. Weathered reject wastes

The fractionation pattern of weathered reject wastes showed that the water soluble fraction pH decreased to about 3.7; thereafter, 31.6% of Co (4.64 mg kg⁻¹), 27.2% of Cu (837 mg kg⁻¹), 44.3% of Mn (75.0 mg kg⁻¹), and 21.5% of Zn (51.5 mg kg⁻¹) were released during this step (Fig. 7E). Gypsum is the most soluble mineral phase in weathered reject wastes, comprising 39% of their mineralogical composition. Exchangeable, acid soluble and Mn oxide fractions exhibit the minimum association with the investigated elements in weathered reject wastes. On the other hand, elements are dominantly associated with other fractions, especially

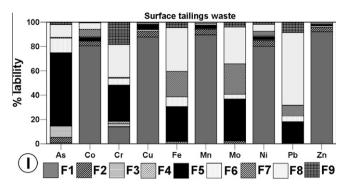


Fig. 7 (continued)

amorphous and crystalline Fe oxides. For example, As is dominantly associated with amorphous and crystalline Fe oxide fractions. These fractions also incorporated 49.4% of Cr, 28.2% of Mo, and 33.1% of Pb. It seems that the most dominant of Co, Cr, Mn, Ni, Pb and Zn concentrations in reject wastes are associated with primary sulfides and residual fractions. As the weathering process and oxidation of sulfide minerals proceed in reject wastes, the remainder of the toxic elements are also released into the environment, although some of the toxic elements like As, Cr, Fe, Mo and Pb can be adsorbed or co-precipitated with amorphous and crystalline Fe oxides. Reject wastes are one of the important sources of AMD in the Sarcheshmeh Cu mine. AMD waters (pH \approx 3) contaminated by high concentrations of Al (39,300 µg/L), Cd (90.4 µg/L), Cu (25,000 μ g/L), Co (485 μ g/L), Mn (27,900 μ g/L), Ni (1140 μ g/L) and Zn (6230 µg/L) are commonly released from these wastes, especially after rainfall.

4.3.4. Tailings

Geochemical analysis showed that the primary composition of tailings changes with time. The total concentrations of some potentially toxic elements are different from one another in tailings samples. For example, Co (367 mg kg⁻¹), Cu (33,100 mg kg⁻¹), Mn (13,100), Ni (348 mg kg⁻¹), and Zn (3830 mg kg⁻¹) are concentrated in the surface crust layer of secondary minerals (Table 4, S8) in dry impoundment samples. These elements are also concentrated in surface tailings (Table 4, S9), but the degree of concentration is lower than the evaporative layers in dry impoundments. Other elements including As, Cr, Fe, Mo and Pb show similar concentrations in surface and sub-surface tailings. It is obvious that geochemical, hydrological and climatological processes have led to some elemental separations of primary tailings. As noted in Sections 4–3, these processes can also result in changes of mineralogical compositions of tailings material.

Chemical fractionation analysis shows that the distribution patterns of metals are very different in tailings samples. For example, 91.8% of Co (272 mg kg $^{-1}$), 93.2% of Cu (31,400 mg kg $^{-1}$), 93.1% of Mn (12,900 mg kg $^{-1}$), 91.1% of Ni (293 mg kg $^{-1}$), 94.3% of Zn (3900 mg kg $^{-1}$) and 34% of Cr (16.2 mg kg $^{-1}$) in the crust layer of secondary minerals (Fig. 7H) are in the form of a water soluble fraction. Arsenic is adsorbed by amorphous Fe oxide (47.2%), carbonate phase (21.8%) and, to a lesser extent, by crystalline Fe oxides (8.81%) in crust layers of old tailings. These fractions are also accompanied by 36.0%, 47.5% and 11.8% of Cr, Pb and Mo, respectively. The remainders of these elements were mainly associated with primary sulfide, oxidizing or residual fractions.

The fractionation patterns of target elements in surface tailings are similar to the surface evaporative layer. However, it seems that the concentrations of elements do not reach the concentrations that are necessary to form secondary minerals. Elements like Co, Cu, Mn, Ni and Zn are mainly related with the water soluble

fraction in surface tailings. After the first step of the fractionation scheme, high contents of Co $(55.6~{\rm mg\,kg^{-1}})$, Cu $(12,000~{\rm mg\,kg^{-1}})$, Mn $(3970~{\rm mg\,kg^{-1}})$, Ni $(58.5~{\rm mg\,kg^{-1}})$, and Zn $(2200~{\rm mg\,kg^{-1}})$ were released from surface tailings into the water (Fig. 7J). Arsenic in surface tailings is mainly adsorbed by amorphous and crystalline Fe oxides $(59.9\%~{\rm and}~12.1\%,~{\rm respectively})$. Chromium, Mo and Pb in surface tailings are mainly adsorbed by amorphous Fe oxides or distributed between oxidizing, primary sulfides and residual fractions.

Potentially toxic elements in sub-surface or fresh tailings (Fig. 7F and G) are mainly associated with oxidizing and primary sulfide fractions. The concentration of nearly all the potentially toxic elements in the water soluble fraction of fresh tailings samples is low or even below detection limits.

It is notable that the exchangeable fraction and Mn oxides show minimum association with potentially toxic elements in nearly all the tailings samples. Manganese hydroxides will generally precipitate at pH 9–9.5 (or even 10 in some cases), but only if the Fe concentration in AMD water is much (more than four times) greater than Mn concentration can Mn be removed from water by coprecipitation with ferric hydroxide (Skousen et al., 1990). In the Sarcheshmeh porphyry Cu mine the Fe concentration in AMD waters is far lower than Mn, and high values of Mn can remain in water even at neutral and alkaline pH values (Table 1). Thus, it is clear that Mn oxy-hydroxides do not have an important role in metal removal from AMD waters.

From the fractionation results it is obvious that with increasing evaporation, the flow direction in dry and inactive impoundments of the Sarcheshmeh tailings pond becomes upward due to capillarity forces. Elements like Co, Cu, Mn, Ni and Zn are concentrated in the top of tailings with more oxidizing conditions, where supersaturating processes control the precipitation of the water soluble secondary salts at the top of the dry impoundments. In the Sarcheshmeh dammed tailings pond, following these changes, the chemical fractionation patterns of potentially toxic elements are also changed. Most of the toxic metals, especially Co, Cu, Mn, Ni and Zn. are incorporated into the water soluble fraction. As shown by Dold and Fontboté (2001), the availability of mobilized metals as water soluble phases makes it necessary to prevent the flush-out of the tailings pond during seasonally strong rainfalls, even in very arid conditions. As noted previously, the mineralogical composition of the tailings evaporative crust layer is mainly comprised of secondary minerals like gypsum, eriochalsite [CuCl₂·2H₂O], bonattite [CuSO₄·3H₂O], and the amorphous materials. These secondary phases are highly soluble and can release high amounts of H⁺ and potentially toxic elements into the water. The role of secondary, especially soluble, hydrous metal sulfate minerals with divalent cations (Me²⁺SO₄·nH₂O) on the release of metals and acidity upon dissolution by rainfall is well documented (Alpers et al., 1994; Jambor et al., 2000; Buckby et al., 2003; Gomes and Favas, 2006).

5. Summary and conclusions

The interpretation of hydrochemical, mineralogical and fractionation analysis of samples associated with mine and processing wastes in the Sarcheshmeh porphyry Cu mine revealed that rock and reject wastes and old tailings are the most important sources of AMD in the water–sediment system. Although the concentration of Pb, Mo and As are very low or even below detection limits in AMD waters, high values of Al, Cd, Cu, Co, Cr, Mn, Ni and Zn are released from wastes into the environment. Therefore, the geochemical behavior of metals such as Cu, Cd, Zn, Ni, Co and Cr are different from As, Pb and Mo in contaminated AMD waters. The various AMD sources have different hydrochemical characteristics. Highly acidic waters containing potentially toxic elements, SO_4^{2-}

and Cl⁻ are produced from tailings over a short period of time. Tailings pond waters are also acidic, like rock waste drainage and reject waste drainage, but the quality of water based on major cations and anions, and also chemical constituents like Mo and Cl in these AMD sources differ considerably.

A wide range of secondary sulfate minerals associated with oxidation of sulfide mineral under AMD conditions were found in studied waste samples. These secondary minerals have important controls on water quality due to release into the water of acidity, metals and non-metal ions, such as SO_4^{2-} and Cl^- . For example, the dominant concentrations of Cl (1690 mg kg $^{-1}$) and Cu (150 mg kg $^{-1}$) in tailings pond water are related to the dissolution of eriochalcite.

Results of chemical fractionation analysis showed that the mineralogical composition of samples is the main factor that controls metal fractionation and its potential release into the environment. Water soluble, carbonate phases and amorphous Fe oxide fractions have maximum association with potentially toxic elements. A distinct relationship was observed between the presence of secondary soluble sulfate minerals and the element contents of the water soluble fraction. For example, samples that contain gypsum, magnesiocopiapite, hydronium jarosite, and coquimbite released high values of As (42.1 mg kg $^{-1}$), Co (82.3 mg kg $^{-1}$), Cr (13.3 mg kg $^{-1}$), Cu (13,400 mg kg $^{-1}$), Mn (1970 mg kg $^{-1}$), Fe (32,920 mg kg $^{-1}$), Ni (58.6 mg kg $^{-1}$), and Zn (783 mg kg $^{-1}$) into the water soluble fractionation phase. Most of the potentially toxic elements and acidity can be stored in secondary minerals, especially in dry seasons, and be released during wet seasons.

Chemical fractionation patterns of potentially toxic elements also revealed that elements like As, Cr, Mo and Pb in efflorescence associated with rock waste drainage, old weathered reject wastes, and evaporative crust layers of tailings are mainly either adsorbed by amorphous and crystalline Fe oxides or distributed between primary sulfides and the residual fraction in fresh unaltered waste samples.

The primary composition of fresh tailings changed in response to a combination of factors, such as oxidation of sulfide minerals and climatic conditions. Following these changes, the mineralogical and fractionation patterns of potentially toxic elements also changed. The chemical fractionation patterns of elements in subsurface tailings were dominated by amorphous Fe oxides, the oxidizing and the primary minerals fractions, whereas in surface tailings and especially in crust layers of the secondary minerals, high contents of Co, Cu, Mn, Ni and Zn dominated the water soluble fraction.

The Sarcheshmeh area is located in an arid climate area and the inadequacy of water dictates that much of the water necessary for the processing plant be supplied from recycled waters of the tailing pond. As a result of the increased volume of the Sarcheshmeh tailings pond and discharges of new tailings over the old dry impoundments, the corrosiveness of recycled water is increased due to the release of acidity and some highly corrosive ions, such as Cl⁻. These changes result in corrosive attack on the pipes and pumps of the water recycling system. Therefore, environmental management of geochemical processes that occur in the tailings pond is necessary not only for the environmental concerns associated with potentially toxic elements and acidity, but also for the subsequent industrial uses of recycled waters. A high content of corrosive ions, such as Cl⁻, as well as high acidity causes damage to the pipes and pumps of the water recycling system.

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